



GE Power Systems

Fine Particle and Precursor Emissions From Power, Oil & Gas Industry Sources

PM_{2.5} and Electric Power Generation: Recent Findings and Implications
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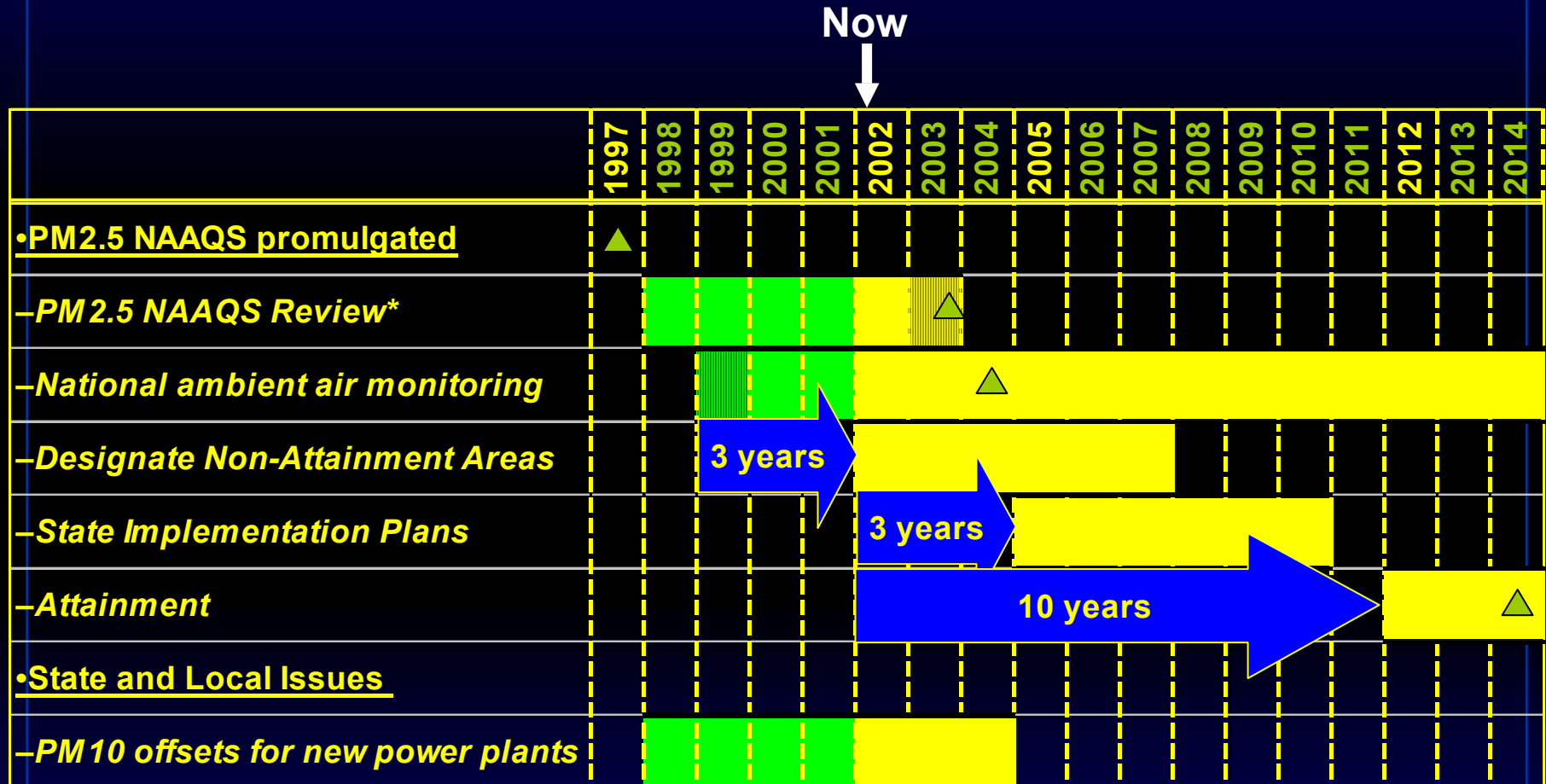
API Contract No. 00-0000-4303



Overview

- **Program background**
- **Measurements and results**
- **Findings and plans**

PM 2.5 Drivers



Sources of Ambient PM2.5

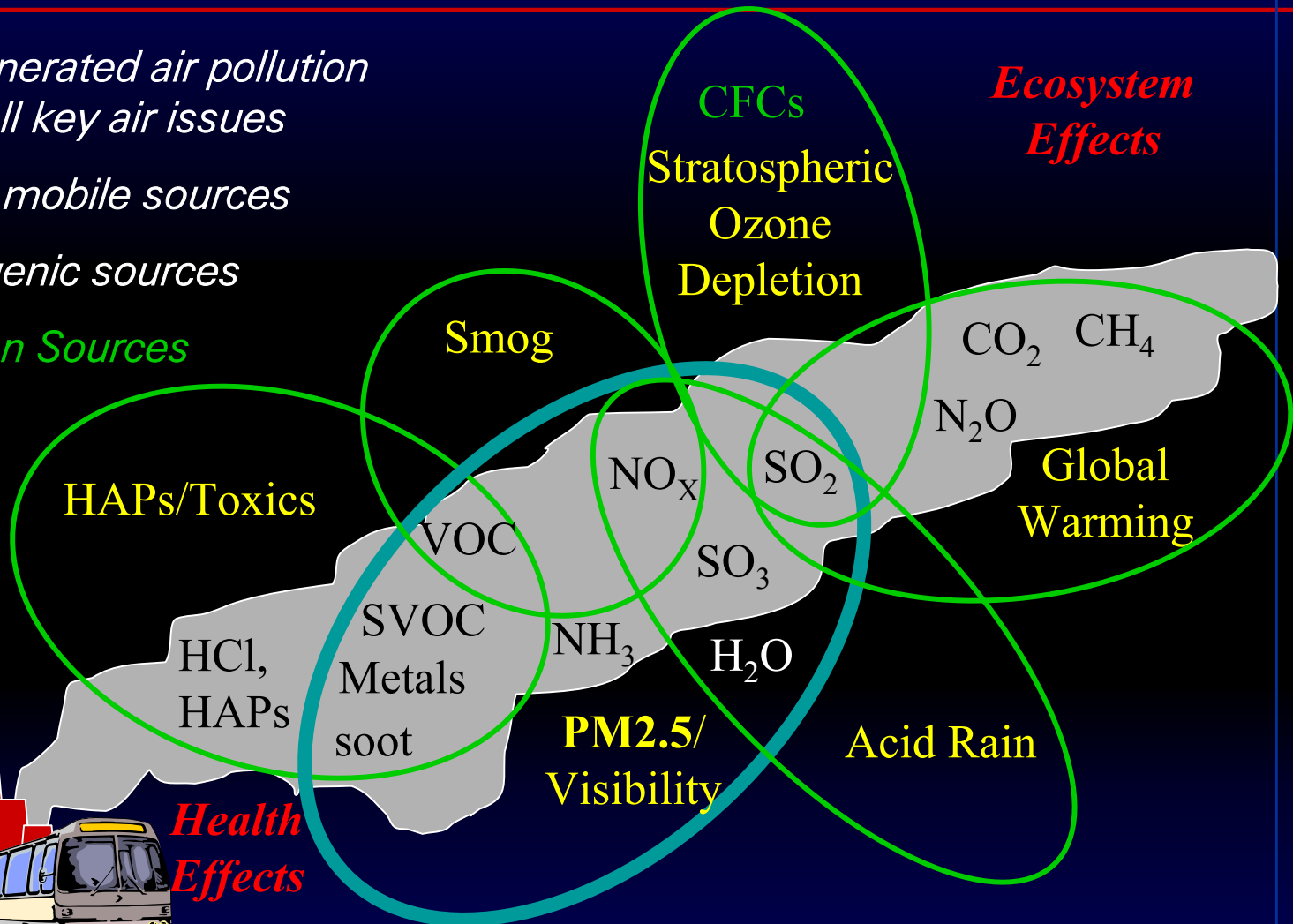
Combustion-generated air pollution encompasses all key air issues

- *Stationary and mobile sources*
- *Non-anthropogenic sources*

Non-Combustion Sources

Relative contribution of different sources?

Combustion processes



The majority of ambient PM2.5 is formed in the atmosphere from precursors which are not particles at the emission point

The Program

Source Apportionment: Need Valid PM2.5/Precursor Emission Factors and Source PM2.5 Speciation Profiles

- **Background**
 - API Critical Review (Q4 1996)
 - API/DOE NPTO refinery heater/FCCU tests (Q3 1998)
 - API/GTI steam generator test (Q3 2000)
 - GTI/NYSERDA/CEC fine/ultrafine PM2.5 test method & sampling project (plan Q1 2000)
 - DOE NPTO/API/GE (Q3 2000)
 - CEC/NYSERDA/GTI and DOE/API projects develop common work scope (Fall, 2000)
- **Improved PM2.5 source characterization data & method development for emission inventory and source apportionment:**
 - Among the ten top research priorities cited by the **National Research Council Committee on Research Priorities for Airborne Particulate Matter** (2000, 2001)
 - PM2.5 emission factors, characterization, chemical speciation
 - A proven test method (based on dilution tunnel)
- **Current Project**
 - Year 1: Definition and data collection
 - **Year 2: Next generation sampler; data collection**
 - Year 3: Data collection; method

Gas Fired Test Units

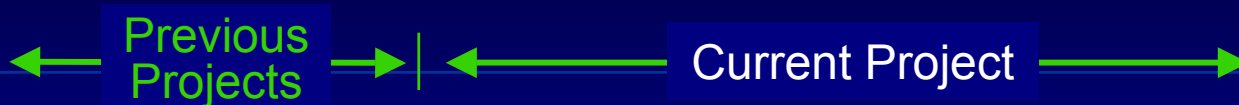
	Site A	Site B	Site C	Site 1	Site 2	Site 3
Unit type	Boiler	Process Heater	Steam Generator	Process Heater	Gas Turbine	Process Heater
Configuration	Tangentially fired	4 radiant wall-fired box-type heaters	Single burner	2 bottom-fired box-type heaters	Single shaft combined-cycle/duct burners cogen unit	2 bottom-fired box-type heaters
Size	650 MMBtu/hr	114 MMBtu/hr	62.5 MMBtu/hr	185 MMBtu/hr	240 MW (2000 MMBtu/hr)	300 MMBtu/hr
APCD	None	None	Flue-gas recirculation	None	DLN combustor, oxidation catalyst, SCR	SCR
Fuel type	Refinery gas	Refinery gas	Natural gas	Refinery gas	Natural gas	Natural gas

← Previous Projects →

← Current Project →

Other Test Units

	Site A	Site 4	GE EER Test Site
Unit type	Refinery FCCU	Dual-Fuel Boiler	Pilot-scale boiler simulator
Configuration	Fluid Bed Catalyst Regenerator + Fired CO Heater	Boiler (hot water)	Furnace + convective section
Size	47,000 bbl/day	165 MMBtu/hr	1 MMBtu/hr
APCD	Electrostatic precipitator	None	None
Fuel type	Refinery gas (heater)	No. 6 oil, natural gas	Natural gas, No. 6 oil, coal



Measurements Overview

Traditional Stack Sampling

PM10, PM2.5, filterable and
Condensable Particulate (cyclones,
heated filter, Impinger train)

NO, NO_x, SO₂, CO, CO₂, O₂
(continuous monitors)

Solid/Condensable Particle size dist.
(dual cascade impactors)

Ammonia (in-stack filter, impingers)

SO₃ (controlled condensation)

Dilution Tunnel

- PM2.5 mass
- Primary particle speciation
- VOC & SVOC
- PM2.5 Size Distribution
- Ultrafines (<0.1 µm)

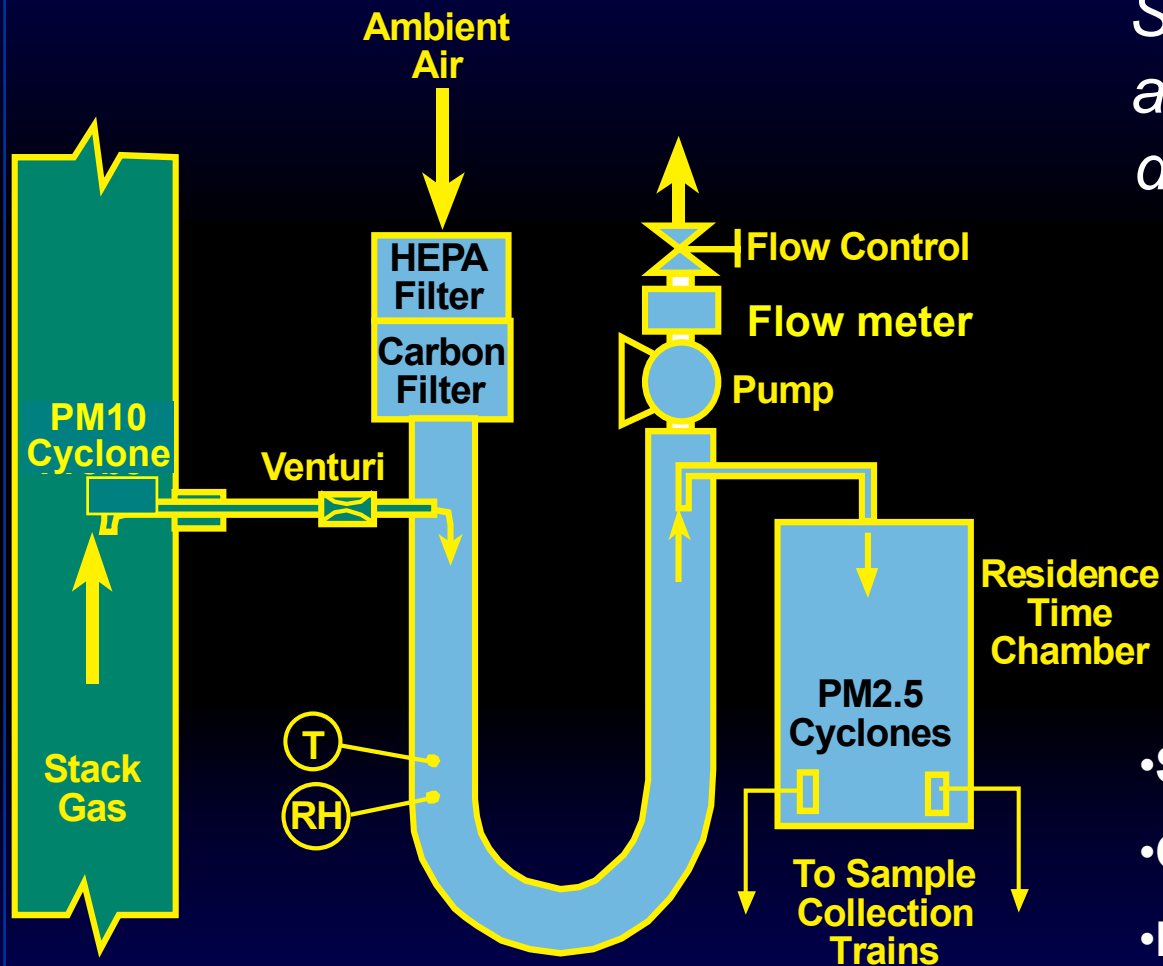
6-hour test runs

Ambient Air and Stack

stack

Combustion
Sources

Dilution Sampler



Sample gas is cooled to ambient temperature by dilution with ambient air

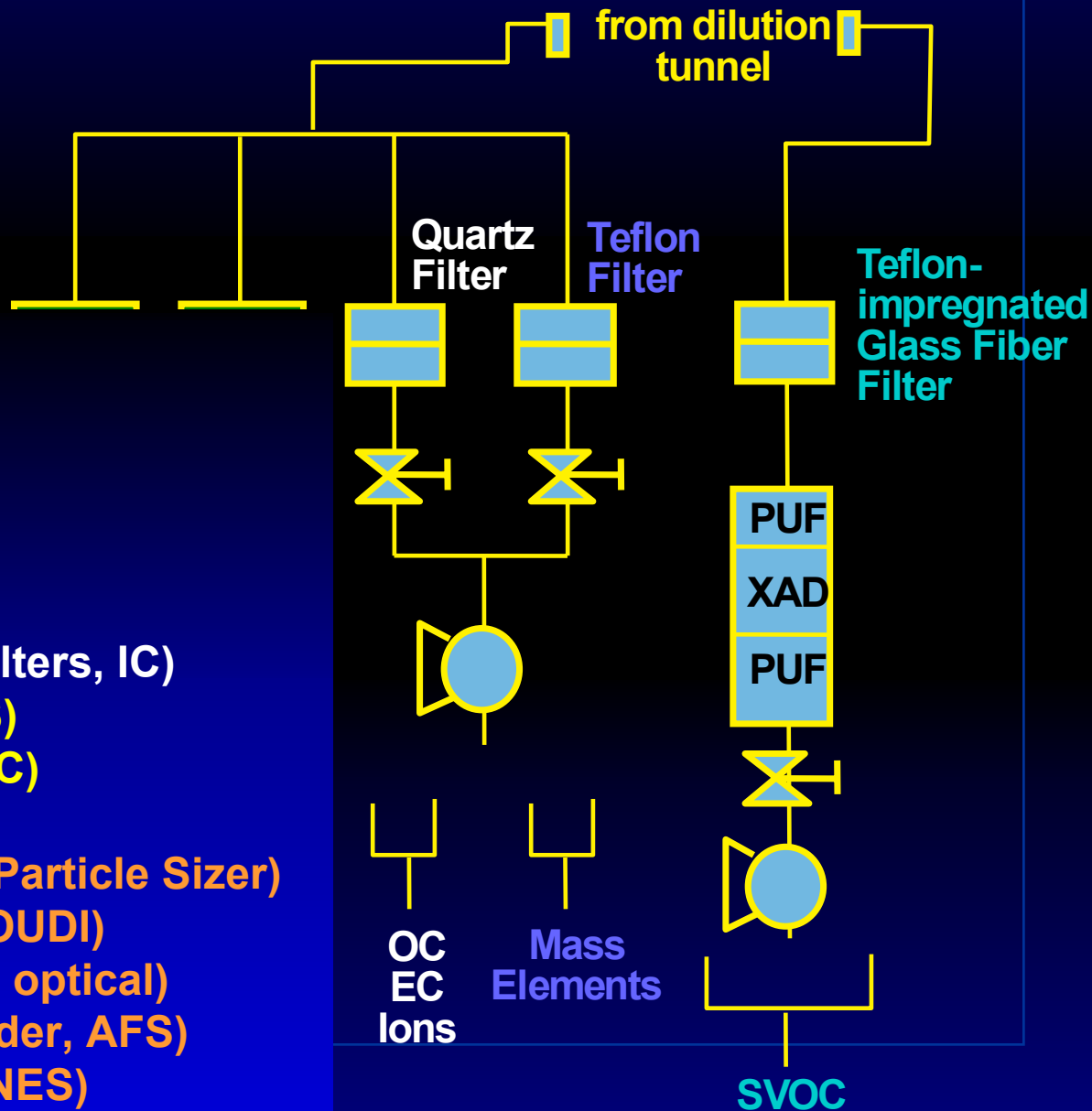
- Stainless steel
- Cross-flow jet mixing
- Dilution Ratio **10-40:1**
- Residence time **80-90 sec**

Dilution Tunnel Sample Collection

- *Ambient air methods assure comparability*
- *Broad range of media and analytical techniques*

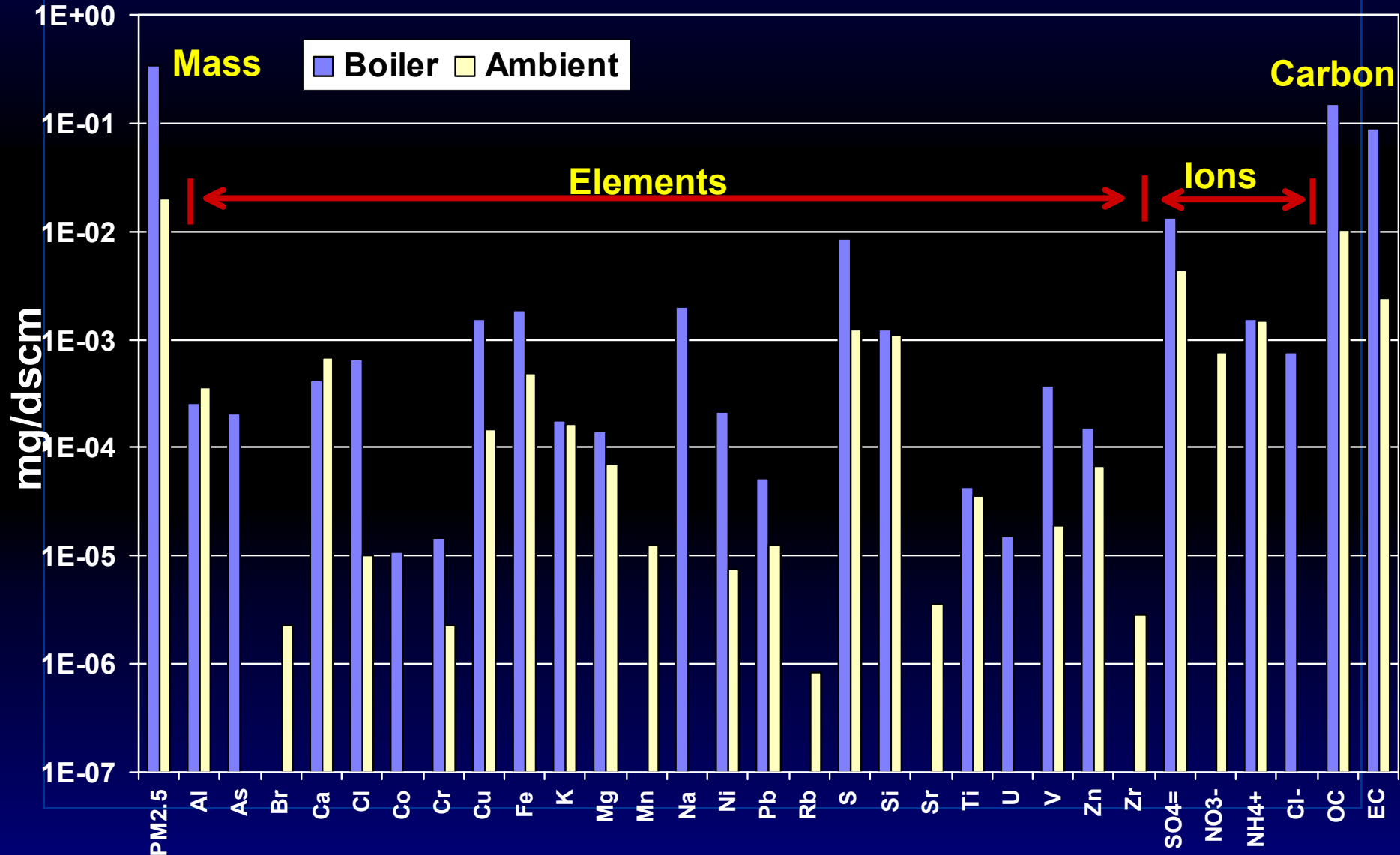
Sample Analysis

- PM_{2.5} mass (gravimetric)
- 40+ Elements Al-Zn (XRF)
- OC/EC (TOR)
- Ions: SO₄⁼, NO₃⁻, Cl⁻ (IC)
- Ammonium (colorimetry)
- SO₂, ammonia (impregnated filters, IC)
- VOC (Tenax/Canisters, GC/MS)
- Carbonyls (sorbent tube, HPLC)
- SVOC (PUF/XAD, GC/MS)
- Ultrafines (Scanning Mobility Particle Sizer)
- Chemically-specified size (MOUDI)
- Real-time PM_{2.5} mass (TEOM, optical)
- Mercury speciation (KCl denuder, AFS)
- Ni, V, Fe speciation (filter, XANES)



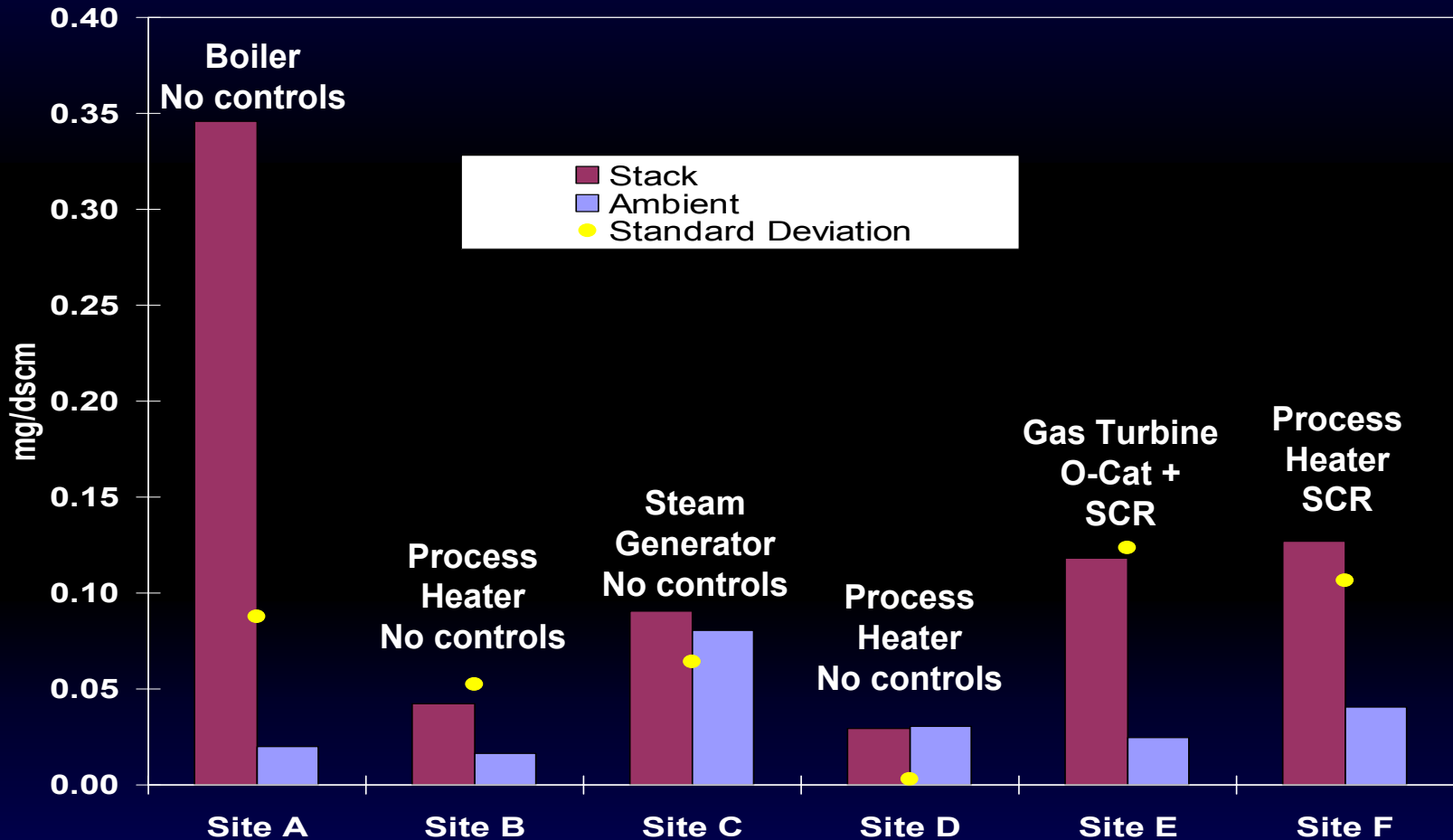
Speciation Profile – Gas-Fired Boiler

- Mass (dilution tunnel)



Comparison to Ambient Air Background

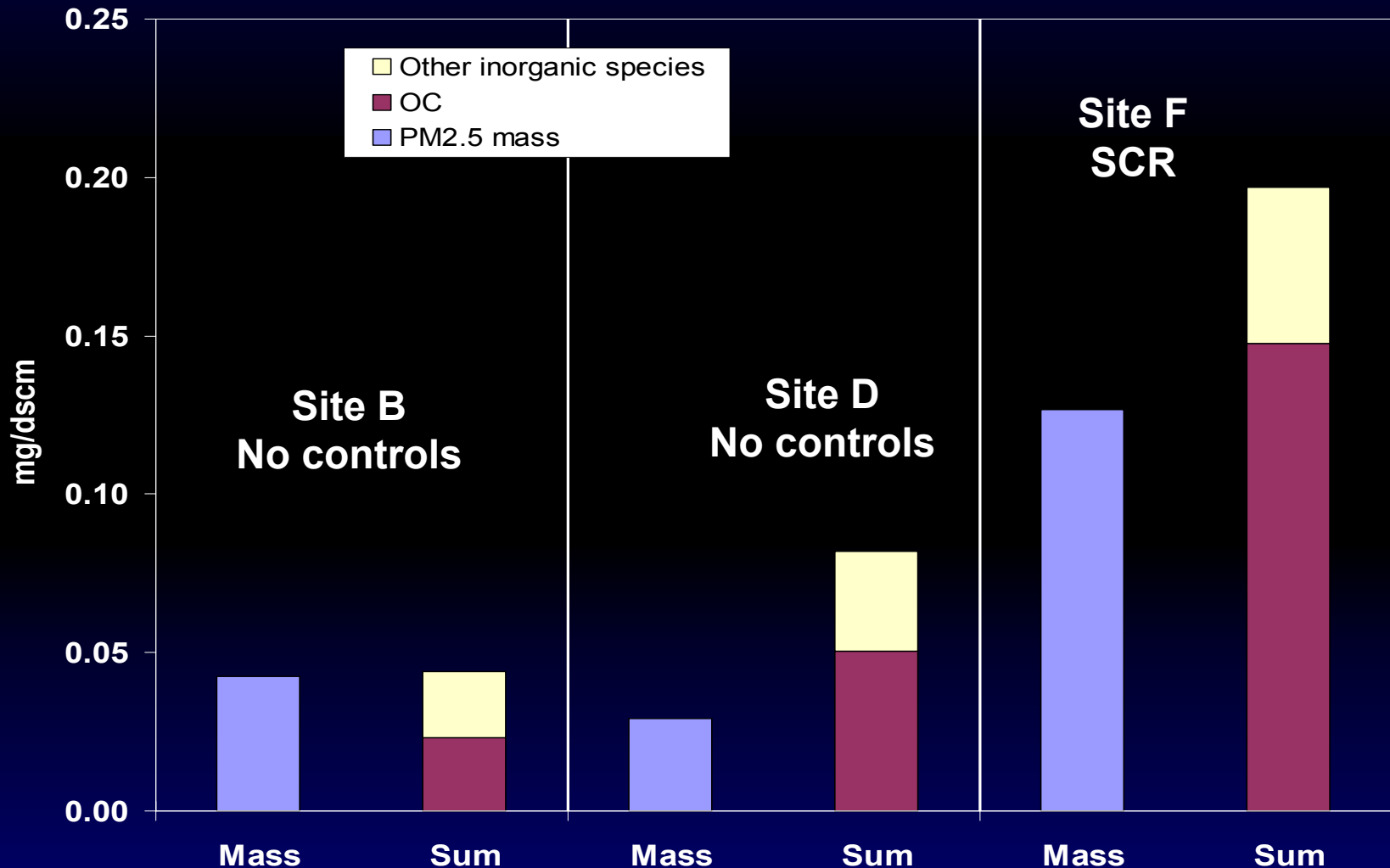
- PM2.5 Mass (dilution tunnel)



In-stack PM2.5 concentration from gas-fired sources is near ambient

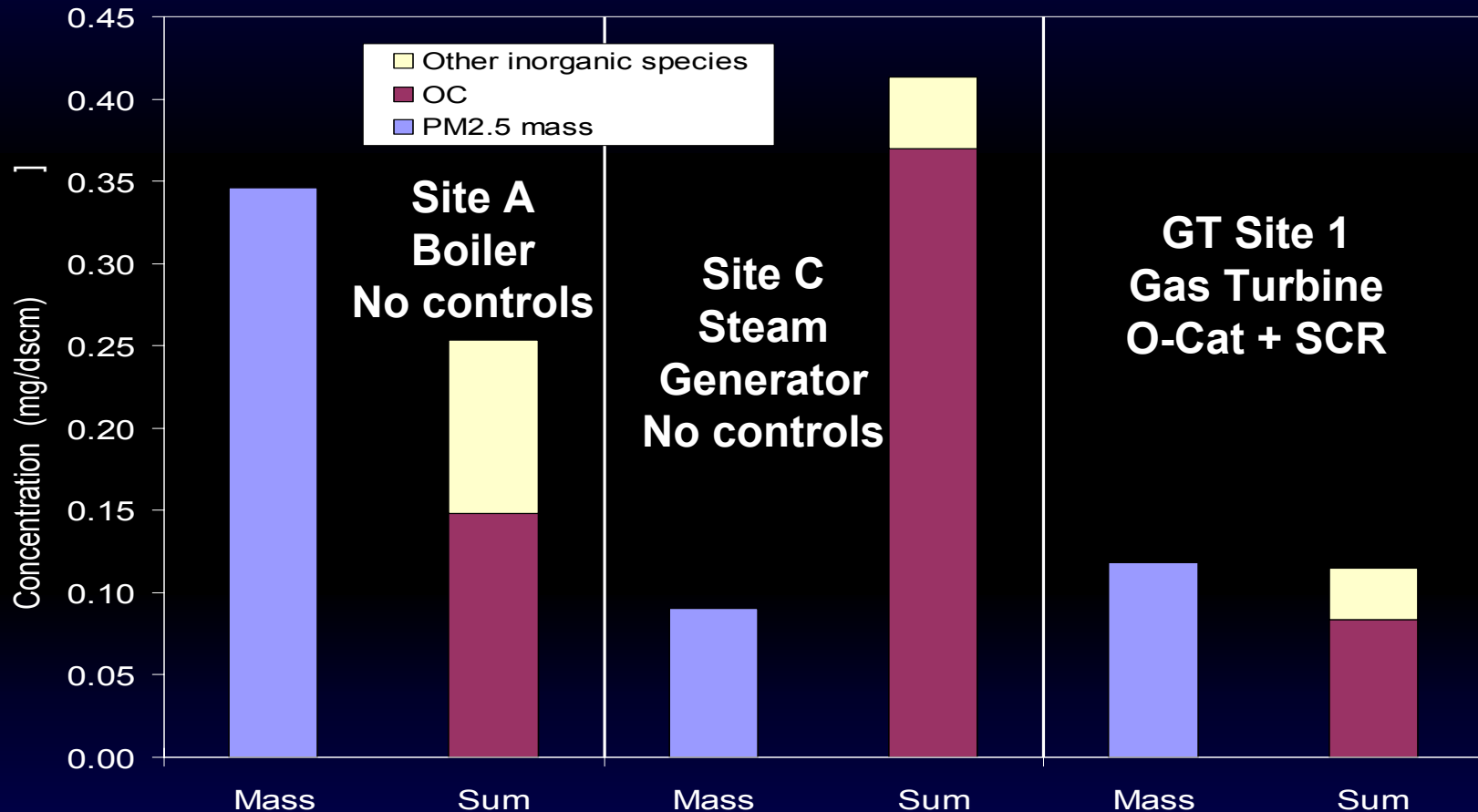
PM2.5 Mass Speciation Closure

- Gas-fired process heaters (dilution tunnel)



PM2.5 Mass Speciation Closure

- Other gas-fired sites (dilution tunnel)



Organic carbon artifact may bias species sum in sources with high organic emissions

Traditional Filter/Impinger Methods

PM10 and PM2.5 cyclones and filter (in-stack)

Glass or Teflon® probe liner (heated)

Teflon® tubing (heated)

Filter

Condensable PM

Filterable PM

Analysis:

- Evaporation of rinses
- Gravimetric analysis

Analysis:

- Organic extraction
- Titration of inorganic fraction
- Gravimetric analysis
- $\text{SO}_4^{=}$ and Cl^-

Post Test Purge with N_2 or Air

Sample gas is cooled to 60-70F in iced impingers

EPA Methods PRE4 & 202

PM10 Methods

- Traditional Source Test Methods

Method	Cyclone	Probe Catch	Filter Catch	Impingers			
				1	2	3	4
PRE-4	PM10 and PM2.5	Yes	Yes	Front-half only			
5	No	Yes	Yes	W	W	E	SG
5i	No	yes	yes	W	W	E	SG
8	Back-half only			IPA	H2O2	H2O2	SG
17	No	Yes	Yes	W	W	E	SG
201A	PM10	Yes	Yes	Front-half only			
202	Back-half only			W	W	E	SG

W - Deionized water

H2O2 - Hydrogen peroxide

IPA - Isopropyl alcohol

E - Empty

SG - Silica gel

Post-test purge:

(Rubenstein, 2001)

Method 8: 10 min air

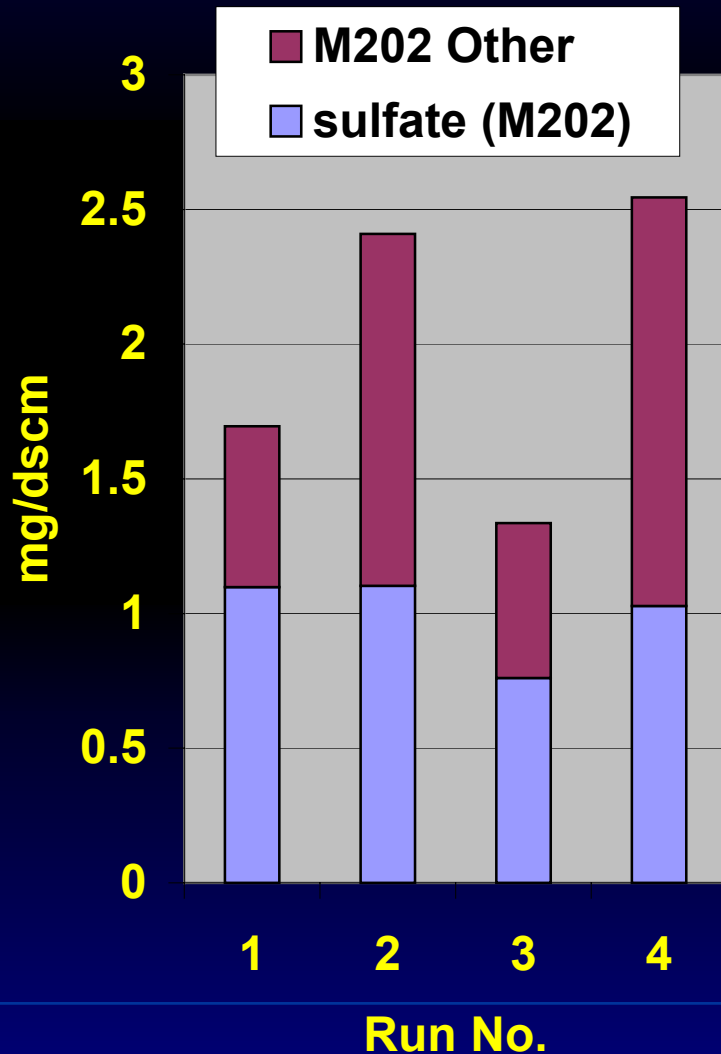
Method 202: Recommended 30 min air or N2 but not required if pH<4.5

Many state/local variations on impinger collection/analysis method

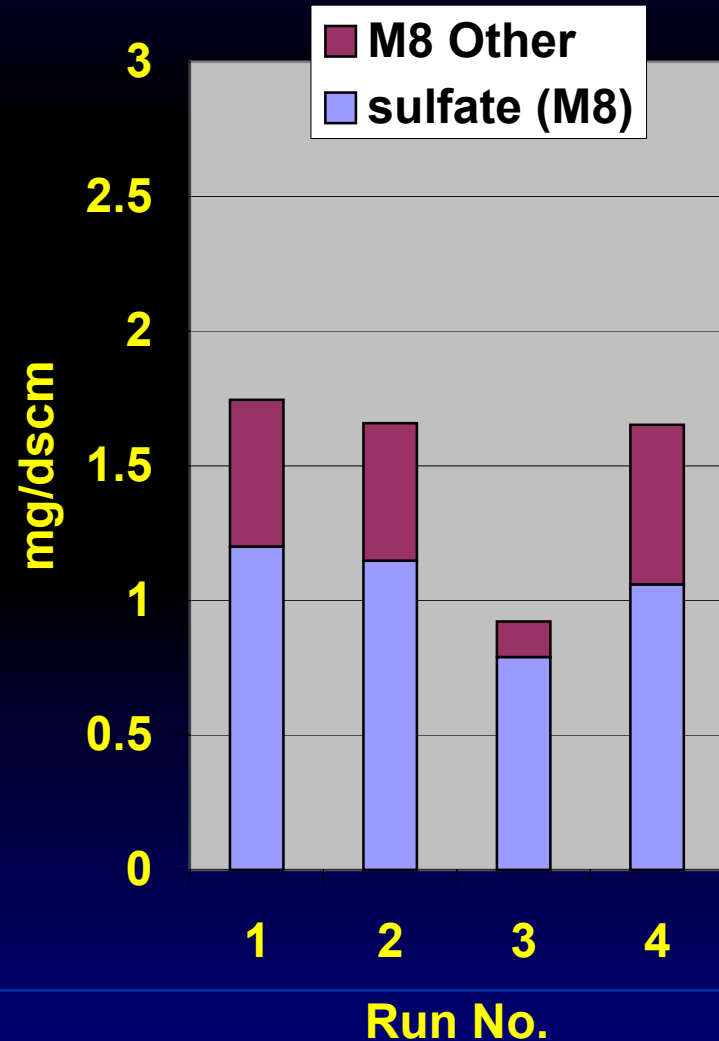
Gas Turbine Condensable PM (Impinger)

- Simultaneous M202 and MM8 sampling trains
- 6-hour runs

M202

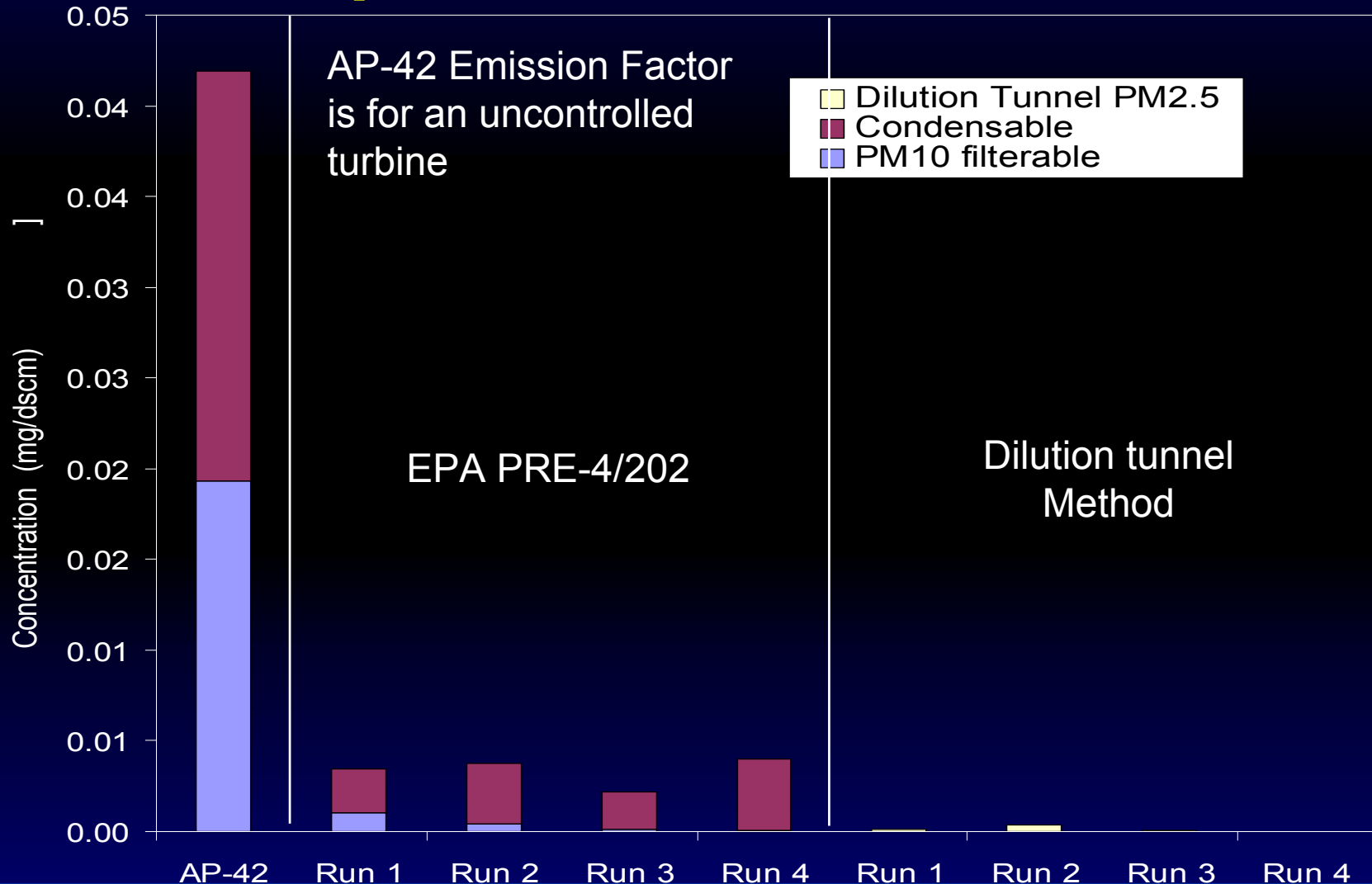


M8



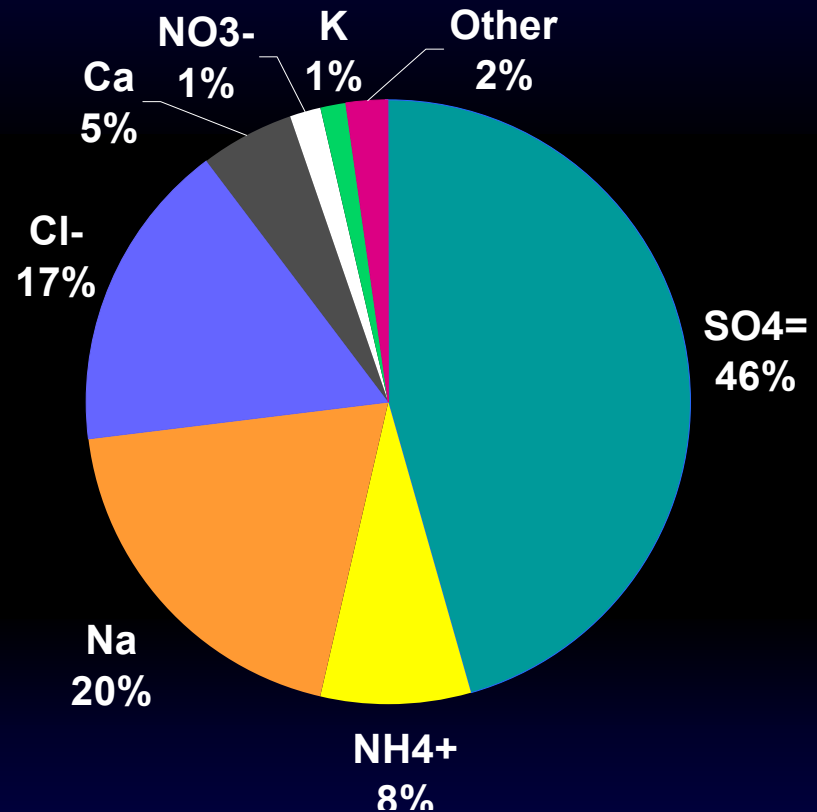
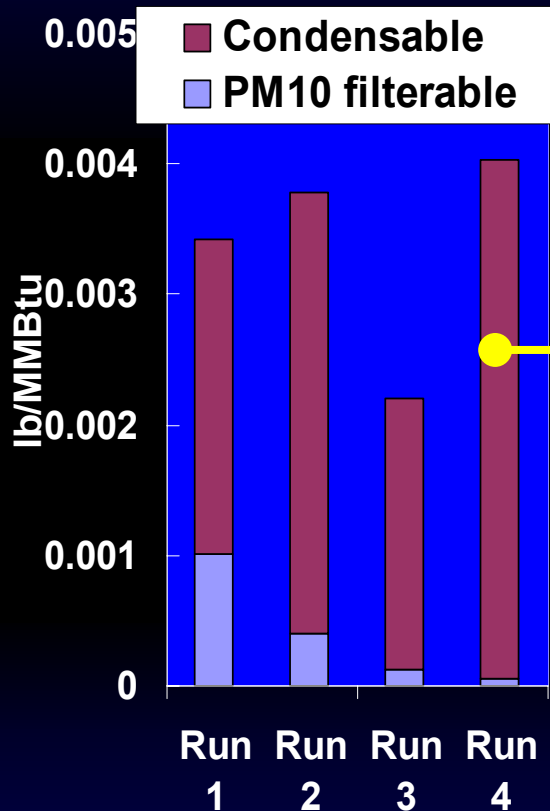
Gas Turbine Emissions – GT Site 1

Method Comparison with AP-42 Emission Factor



Gas Turbine PM10 Emissions

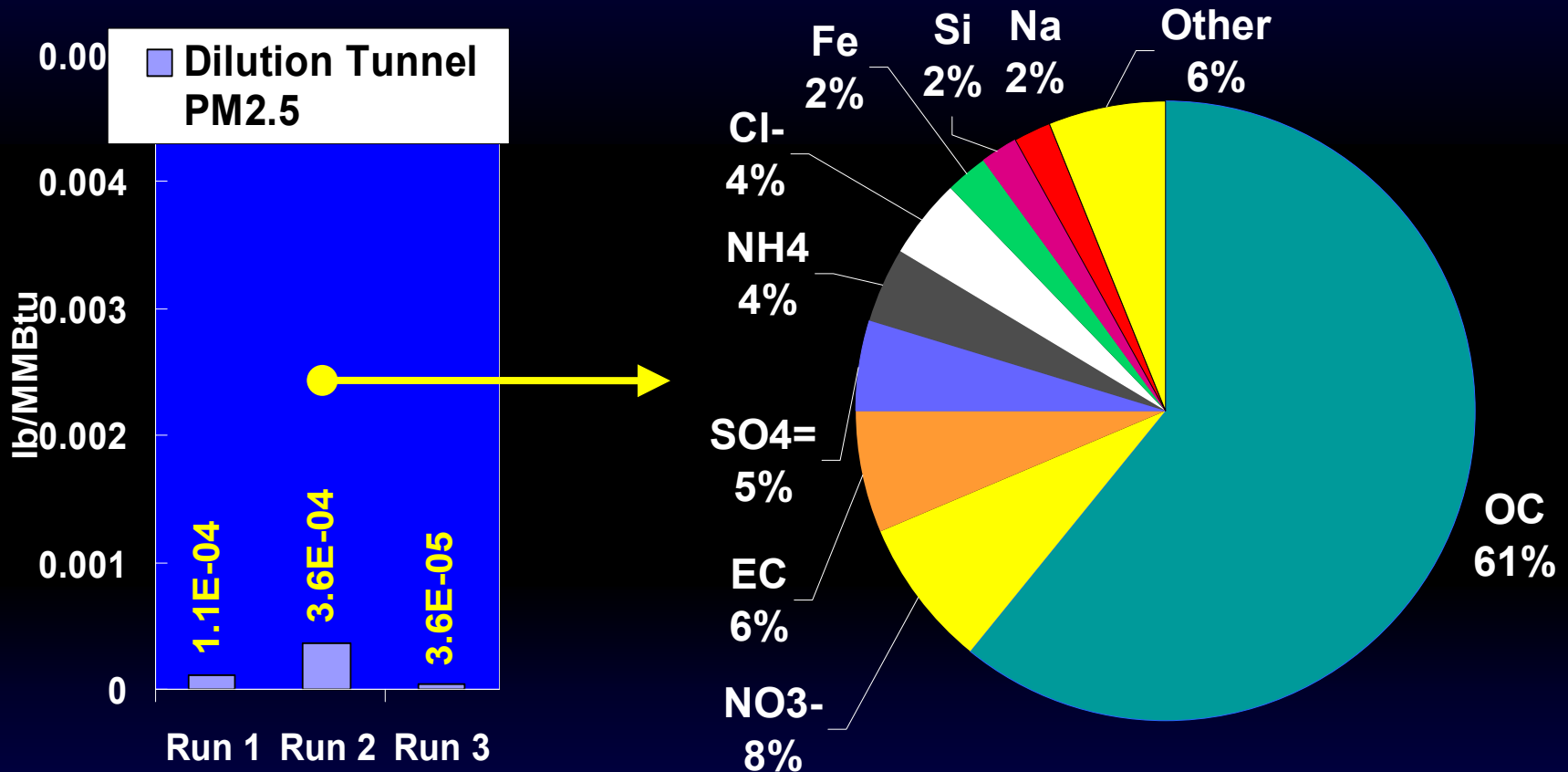
- Condensable PM (M202) Residue Speciation



- The majority of PM10 is PM2.5
- Sulfate is largest fraction of CPM mass

Gas Turbine PM2.5 Emissions

- Dilution tunnel PM2.5 speciation



Carbon is majority of PM2.5 mass measured by the dilution tunnel

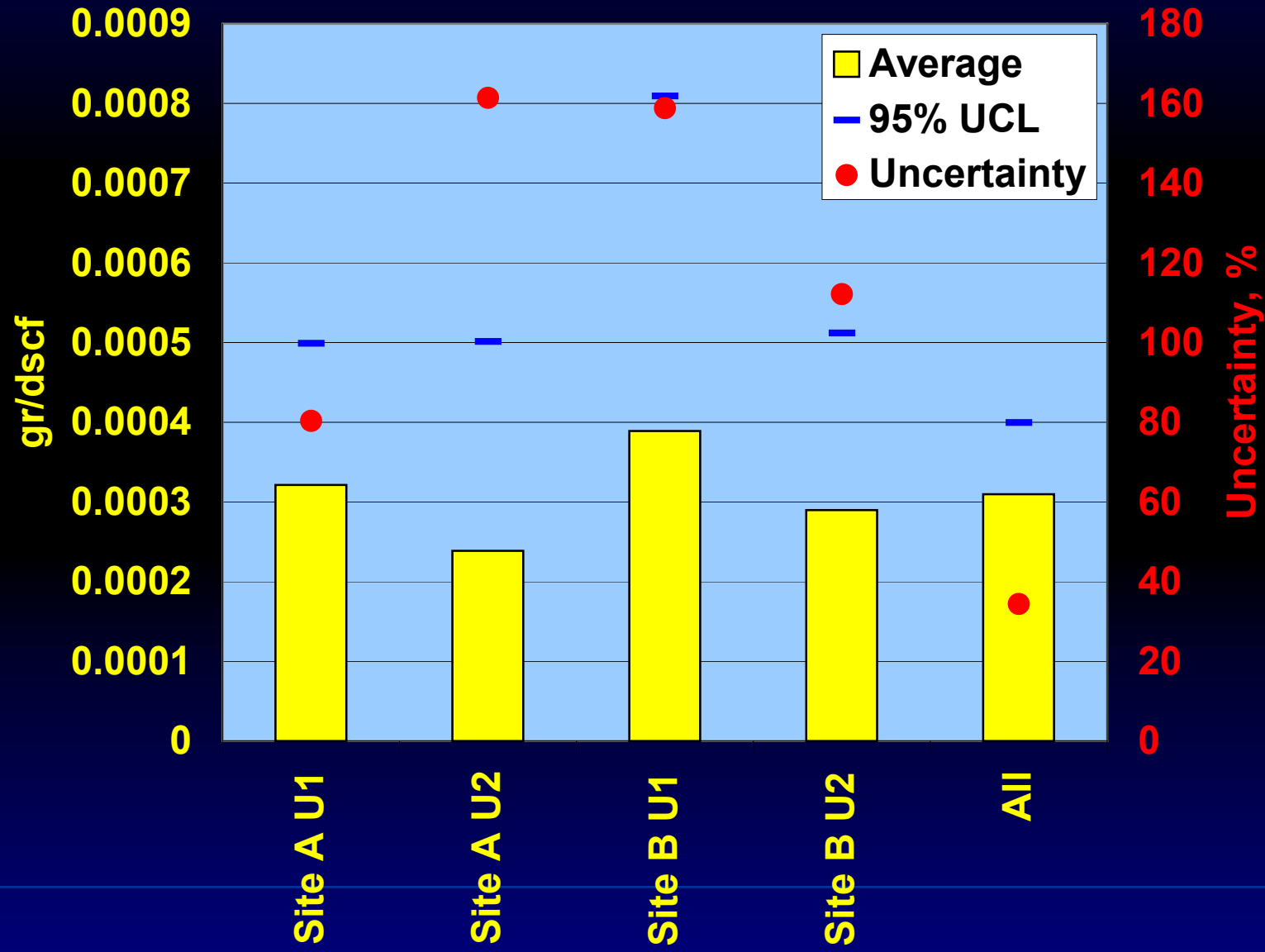
Measurement Artifacts

- Impinger method positive bias from SO₂ oxidation to sulfate
 - Sulfur in natural gas significant relative to PM
 - Artifact increases with time and SO₂ concentration
 - Minimize by post-test purge with N₂
- Fundamental difference between current stack test and dilution tunnel methods
 - Aerosol nucleation driven by saturation ratio
 - Impinger method cools without changing concentration
 - » High saturation ratio leads to more condensation
 - Dilution tunnel (and stack plume) cools with decreasing concentration
 - » Low saturation ratio leads to less condensation
- Dilution method
 - Positive OC bias from VOC
 - Negative PM mass bias from losses in tunnel

Dilution tunnel provides results more representative of plume than traditional methods

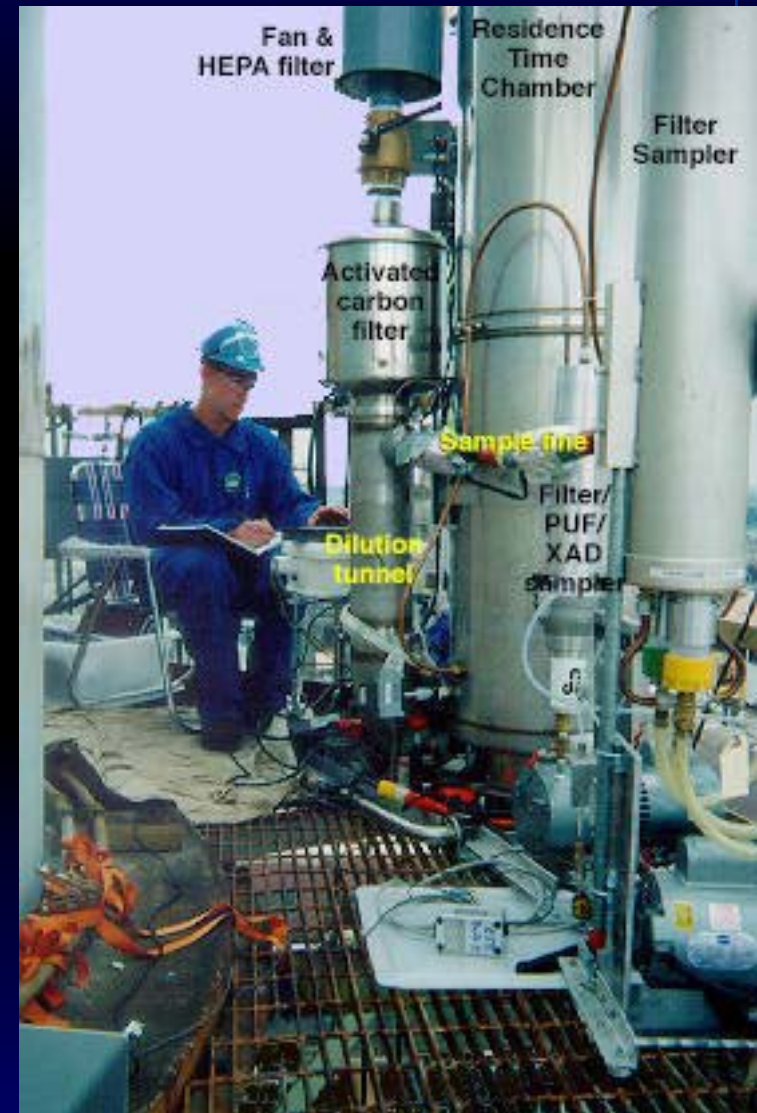
PM10 Emissions – Gas Turbines

- EPA Method 202 Results



Dilution Tunnel Issues

- **Successfully applied to 9 diverse sources**
 - Gas, oil, and coal
 - Comprehensive inorganic and organic chemical speciation profiles developed
- **Current size limits applications to units with adequate platforms**
 - Traversing impractical
 - Costly
- **Future development underway for use as routine test method**
 - Design parameters for different applications
 - » Pilot-scale combustion tests
 - » Comparison to other dilution systems
 - Consensus standard adoption
 - Better-SMALLER-faster-cheaper



Findings – Gas Turbines – EPA Methods

- Improved method techniques reduce PM₁₀ variability
 - 4-6 hr sampling time
 - PM₁₀ cyclone on probe (to remove spurious large particles)
 - Post-test nitrogen purge
 - Use all Method 202 analytical options
 - Other data and QA/QC improvements
- Results from single test:
 - typically near or below method MDL (3 sigma)
 - Always below PLQ (10 sigma)
 - Uncertainty always >100% of result (95% confidence)
- Method 202 vs. Modified Method 8
 - Sulfate results very similar
 - Non-sulfate slightly greater with M202
 - Modified Method 8 looks promising
- SO₂ artifact leads to significant sulfate bias for natural gas combustion
 - Post-test purge helps but doesn't eliminate artifact

Findings

- Extremely low PM concentrations in gas-fired sources challenge the limits of all current methods
- The condensable portion of primary PM_{2.5} may be overestimated using impinger-based methods
 - Sulfate artifacts significant even for gas-fired sources
 - Aerosol formation and growth is a function of both cooling and concentrations
- Improved protocol for dilution methods necessary for both emission factors and chemical speciation

Different test methods give very different results!

Dilution tunnel results best for source apportionment and source-receptor modeling

Don't mix emission factors from traditional methods with speciation from dilution methods

Next Steps

- **Advanced dilution sampler design and construction**
 - **Pilot-Scale Tests**
 - » Develop design criteria and improve procedures
 - » Compare dilution tunnel designs
 - **Evaluate additional characterization techniques**
 - » Ultrafines (SMPS/DMA)
 - » Real-time monitoring (TEOM)
 - » Denuders to reduce artifacts

Next Steps (cont'd)

- **Additional Field Tests**
 - Gas turbines (power generation)
 - Oil-fired utility boiler?
 - Pipeline compressors
 - » Reciprocating and gas turbine engines
 - Distributed power generation
 - Expand characterization (HAPs, other key substances)
 - » Ultrafines, mercury, N-PAH, carbonyls, metal species
- **Refine data analysis and findings**

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